

STRUCTURE AND STRUCTURAL DIVERSITY IN RESINITES AS DETERMINED BY PYROLYSIS-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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INTRODUCTION

A number of workers have reported data concerning the analysis of fossil resins,¹⁻⁷ (often referred to as "amber", but referred to herein by their correct general geologic name - resinite). It has become apparent from these data, that a number of chemically distinct forms of resinite exist in the geosphere. At present however, no convention exists for the differentiation of these chemically distinct materials. This problem of nomenclature is further compounded by a degree of ambiguity in the petrographic identification of resinites⁸, and also by the inappropriate use of the term "resin" to describe certain petroleum and source rock components. As a result, the literature concerning the geochemistry of higher plant resins is somewhat confused.

General structural characteristics of a number of different resinites have been established by previous studies. Results of analyses carried out in our laboratory however, indicate that even within closely related samples, a significant degree of variability of composition exists, often as the result of differences in botanical origin and/or level of thermal maturity. We have therefore sought to develop a classification system for resinites, and to establish criteria by which individual resinites may be unambiguously classified.

In order to investigate the nature and extent of variability in resinite structure, we have sought to establish a broadly based resinite sample collection. The results of Pyrolysis-Gas Chromatography-Mass Spectrometric (Py-GC-MS), analyses of a number of different resinite samples from this collection, and the implications of these results to the nomenclature and classification of resinites, are described herein.

EXPERIMENTAL

Py-GC-MS analyses were carried out using an HP-5890 GC coupled with an HP-5970 MSD. Resinite samples (approx. 1 mg) were subjected to pyrolysis in the presence of excess tetramethylammonium hydroxide (TMAH) to effect in-situ methylation of acidic components,⁹ using a C.D.S. "pyroprobe" coil type pyrolyzer. 60m DB-5 and DB-1701 columns were used to obtain adequate chromatographic separation of components.

RESULTS AND DISCUSSION

A thorough review of the literature, and the results of analysis of our own carefully screened suite of true resinite samples, suggests that three basic structural families of resinites predominate in the geosphere. A small number of less common forms are also known, but are usually restricted to a very small number of sites. The results of Py-GC-MS analyses of examples of each of these resinite classes, illustrated in Figure 1, clearly reflect the compositional differences reported by previous authors. These data also demonstrate that Py-GC-MS is a useful technique for providing detailed information concerning the molecular composition of resinites, especially when used in conjunction with in-situ methylation procedures. As a consequence of these observations, (and parallel spectroscopic data) a preliminary classification system, outlined in Table I and described in detail below, has been developed to rationalize and clarify the nomenclature of resinites, and to enable

researchers to conveniently indicate the specific chemical nature of resinite samples with which their work may be concerned. A more comprehensive description and justification of this classification system will be reported elsewhere.

In addition to resins with structures related to the resinite structures described below, modern plant genus produce numerous other resins, with diverse structural characteristics and compositions. The apparent absence of these resins from geologic strata of significant age however, suggests that these resins are unable to survive diagenetic and/or catagenetic processes in a recognizable form, except perhaps in specialized, rare circumstances.

Class I resinites, which appear to be by far the predominant form of resinite in the geosphere, have been shown by a number of previous workers to be polyditerpenoid structures, based predominantly on the 14,15- polymerization products of labdatriene carboxylic acids, especially communic acid or zanzibaric acid (structures I-IV below).¹⁻⁶ Other mono and diterpenoids are often incorporated (or physically occluded) in the structure to a lesser extent. Whilst the results of our analyses concur with these reports, our data indicate that the specific composition of class I resinites, as assessed by Py-GC-MS, varies significantly between samples, and reflects both the botanical origin and maturity of the resinite.

Class I resinites, unlike class II and III resinites which appear to have specific botanical origins, appear to be derived from a number of paelobotanical sources (see Table I). Modern analogues of class I resinites are produced, often in large amounts, by a number botanical genus, including: Araucariaceae, Taxodiaceae, Leguminosae,¹⁰ Cupressaceae,¹¹ and possibly others. This diversity of sources and often copious production probably accounts for the observed predominance of class I resinites in geologic samples.

Py-GC-MS data (illustrated in Figure II) and other results, suggest that class I resinites may usefully be further divided into divided into three sub-classes on the basis of molecular composition. Resinates based on polycommunic acid can and should be distinguished from those based on polyzanzibaric acid, and for some purposes it may also be useful to further divide communic acid based class I resinites into succinylated and non succinylated forms. A number of class I resinites, including "Baltic amber" (succinite), which together comprise probably the single largest source of resinite, incorporate succinic acid as a cross-linking agent between occasional communal units incorporated into a communic acid based polymeric structure. In other communic acid based class I resinites however, succinic acid is absent, suggesting a related but distinct origin for these materials. These finer sub-categories are useful for distinguishing related resinates of distinct botanical origins, and may also aid in establishing correlations between geographically dispersed samples of closely related structural character. Class I resinites may therefore be sub-divided according to the basic character of the polymeric structure as follows: I(a) Succinylated polycommunic acid; I(b) Non-succinylated polycommunic acid; and I(c) polyzanzibaric acid.

Notable features of the chromatograms illustrated in Figure II are: (i) Significant differences in the distributions of intact diterpenoids (eluting between 55 and 70 minutes in these chromatograms), which reflect the different botanical origins (and possibly also the thermal maturities) of the samples, and (ii) the presence of abundant dimethyl succinate in the pyrolysis products of the class Ia sample. This compound is not observed in the pyrolysis products of class Ib or Ic resinates. A more comprehensive analysis of these data will be presented elsewhere. Slight, but highly significant differences are also observed in the nature of the products eluting between 30 and 55 minutes in these chromatograms. These compounds are predominantly bicyclic carboxylic acids derived from the labdanoid ring system of the parent acids. Preliminary data suggest that differences in these products may be useful for distinguishing class Ia and Ib resinates from class Ic resinates in mature samples, in which no detectable intact diterpenoids remain.

Class II resinates have been shown to be based on polymers of sesquiterpenoid hydrocarbons related to cadinene (V).^{6,12,13} Although less common overall than Class I resinates, Class II resinates are very abundant in several locations throughout the world, including the U.S. (specifically Utah) and S.E. Asia (where both modern and fossil deposits occur) and constitute a major resource of resinite. This class of resinite is known to be derived from trees of the Dipterocarpaceae, especially Shorea, modern resins of which, known as Damar, are still commercially exploited, and differ little in structural terms from Class II resinates. Class II resinates are very easily distinguished from Class I and III resinates by pyrolytic techniques (See for example Figures I) on the basis of the nature of the pyrolysis products, especially the absence of significant amounts of carboxylic acids. Spectroscopic data is also often definitive for the classification of resinates of this class.

Class III resinites, which are composed almost entirely of natural polystyrene (VI), are the least common of the three resinite classes defined in Table I, currently identified deposits being restricted to the Eastern US and (possibly) Germany^{7,10}. These resinites are believed to be derived from the resins of *Hammeliaceae*, especially *Liquidambar*. Class III resinites are very easily recognized and classified on the basis of spectroscopic and/or pyrolytic data; the principle problem associated with recognition of these materials being confirmation of the provenance of the sample (ie: being sure that the sample is not synthetic polystyrene which has inadvertently been collected as fossil material).

Class II and III resinites are also distinct from Class I resinites in that resinites of these classes are soluble in organic solvents, and hence may be recovered and concentrated by extraction.

As indicated above, although all resinites of a given class share a number of common structural characteristics, the composition of volatile and volatilizable materials produced by pyrolysis varies considerably between samples. These differences reflect variations in the composition of the original resins, and also differences in the thermal maturity of the samples. These differences are particularly important in class I samples, due to the diversity in the botanical origins of these resinites, but are also likely to be important in other resinites.

In immature class I samples, such as those illustrated in Figure 11, abundant, intact diterpenoids are released by volatilization and thermal depolymerization as a result of pyrolysis. These diterpenoids probably reflect the composition and nature of the original resin and hence are of considerable interest. With increasing thermal maturity however, the significance of these compounds decreases, and substituted unsaturated bicyclic carboxylic acids become increasingly predominant in the pyrolysis products. This probably reflects semi-random cross-linking, especially between olefins, and double bond migration to thermodynamically more stable isomers. This results in a thermally more stable polymeric structure, which is less able to thermally "unzip", and which therefore cleaves off naphthenic structures derived from the labdanoid ring system of the precursor, in this case communic acid. The low abundance of tricyclic products in the pyrolyzate of mature resinite samples suggests that cyclization reactions are not an important maturation process in resinites. At high levels of maturity aromatization and elimination of substituents also appear to be significant. This trend is demonstrated in Figure 1, which illustrates Py-GC-MS data for a series of class Ib resinites obtained from New Zealand coals of known maturity. Similar trends are observed in other class I resinites.

CONCLUSIONS

Py-GC-MS is a useful technique for the rapid characterization of resinites, especially when used in conjunction with in-situ methylation procedures, which permit chromatographic analysis of acidic components without complex sample preparation.

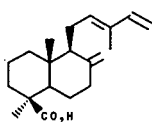
Although significant diversity exists in resinite structures, the majority of resinites may be classified into one of three basic structural groups. Resinites from the largest and most important of these may be further subdivided on the basis of specific structural characteristics into three subclasses. Within these classes, details of specific composition may vary significantly between samples as a consequence of differences in botanical origin and/or level of maturation, but sufficient common structural characteristics exist within these classes to validate application of such a classification system.

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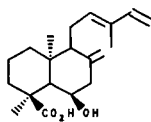
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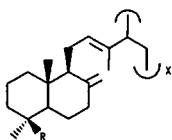
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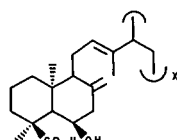
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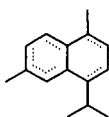
II



III



IV



V



VI

Structures indicated in text: I - Communic acid (trans isomer). II - Zanzibaric acid (trans isomer). III - Basic polymeric structure of class Ia and Ib resinates. (i) R = COOH (polycommunic acid), (ii) R = CH₂OH (may be succinylated ie: CH₂O-CO-(CH₂)₂-CO-O-R'; R'=H or communol unit of polymer.). IV - Basic polymeric structure of class Ic resinates, polyzanzibaric acid. V - Cadinene (dotted lines indicated double bond isomers). VI - styrene.

TABLE I.

Class I

- (a) Basic structural character = polycommunic acid, partially copolymerized with communol. Significant incorporation of succinic acid, probably as a cross linking agent is characteristic.

examples = Succinite (Baltic Amber)

- (b) Basic structural character = polycommunic acid, with varying degrees of copolymerization with communol. Succinic acid is absent.

examples = New Zealand resinites, Victorian Brown Coal resinites.

- (c) Basic structural character = polyzanzibaric acid.

Nearest equivalent modern resins: "Copal" esp. Pontianak, Kauri Resin, Manila Copal
Brazil Copal, Congo Copal

Most probable botanical affinity*: (i) Araucariaceae (esp. Agathis)
(ii) Leguminosae (esp. Hymenaea)
(iii) Cupressaceae, and possibly others.

Class II

Basic structural character = polymer of bicyclic sesquiterpenoid hydrocarbons, esp. cadinene, possibly with some triterpenoid component also present.

examples = Utah resinites, (some) Indonesian resinites.

Nearest equivalent modern resin: "Damar"

Most probable botanical affinity*: Dipterocarpaceae (esp. Shorea)

Class III

Basic structural character = Polystyrene

examples = (some) New Jersey resinites, Montana resinite

Nearest equivalent modern resin: "Storax" (Sometimes = Styra)

Most probable botanical affinity*: Hammelidaceae (esp. liquidambar)

*Based on equivalent modern resins.

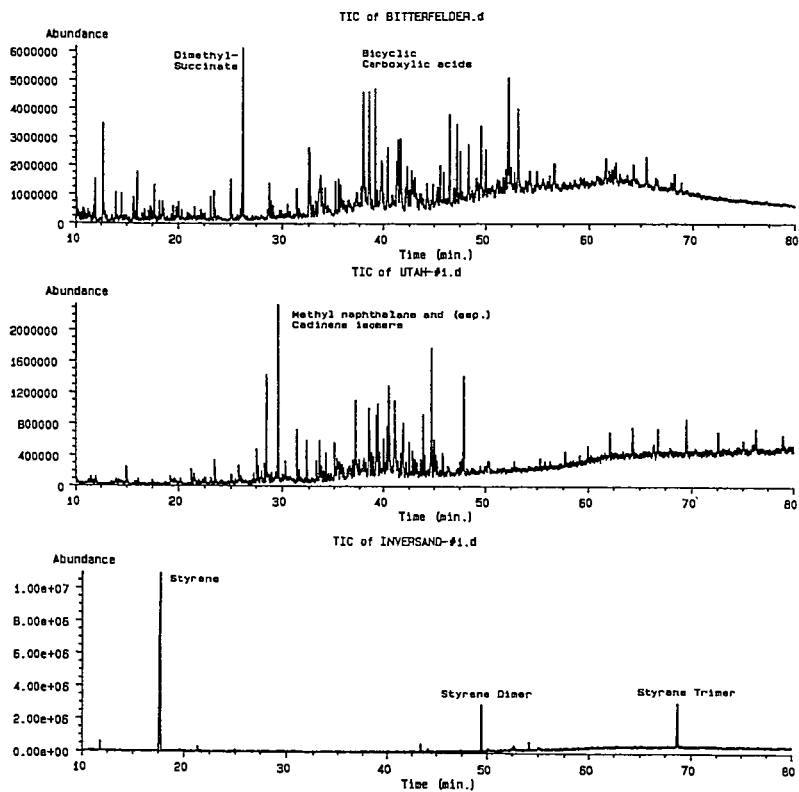


Figure I. Py-GC-MS data for typical examples of Class Ia, II and III resinites. Top: CLASS Ia - Bitterfelder resinite (Germany) [AMNH # B-3]. Centre: CLASS II - Blind Canyon resinite (Utah, U.S.A.). Bottom: CLASS III - Sayrville resinite (New Jersey, U.S.A.) [NJSM #14156]. $T_{\text{pyrolysis}} = 540^{\circ}\text{C}$, Column = 60m DB-1701.

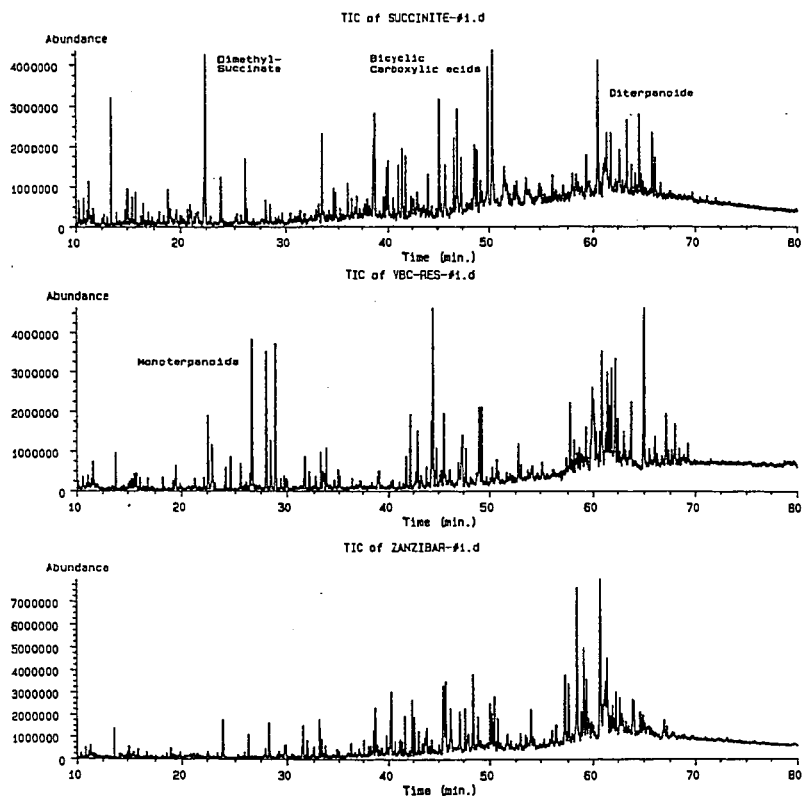


Figure II. Py-GC-MS data for class Ia, Ib, and Ic resinites. Top: Succinite, Baltic region, Eastern Europe [USNM #353431], Centre: Victorian Brown Coal resinite, Latrobe Valley, Victoria, Australia Bottom: Zanzibar resinite, Zanzibar, Africa [AMNH # H252]. $T_{\text{pyrolysis}}=480^{\circ}\text{C}$, Column = 60m DB-5.

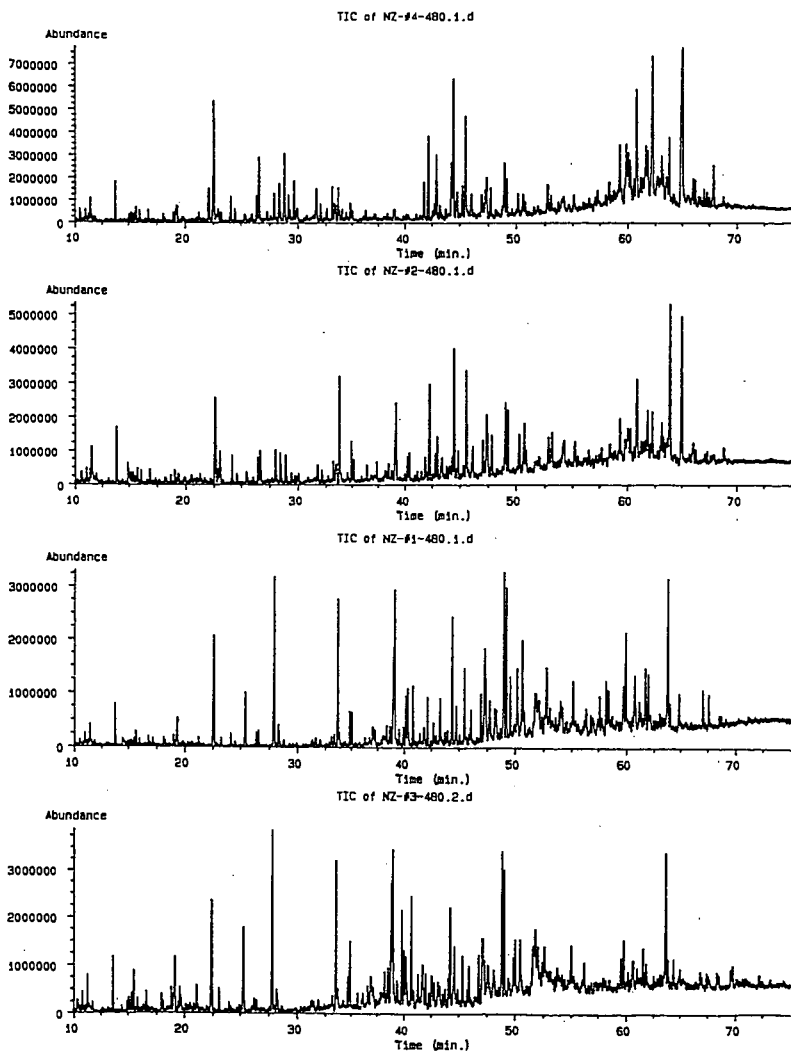


Figure III. Py-GC-MS data for New Zealand Class Ib resinites, showing changes in pyrolysis product distribution as a consequence of increasing thermal maturation.
 $T_{\text{pyrolysis}} = 480^{\circ}\text{C}$, Column = 60m DB-5.222